

Speciation of Zn and Ni in soil micronodules by X-ray microfluorescence and microdiffraction

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INTRODUCTION

A molecular-level understanding of the form of toxic metals in natural systems offers a scientific approach to cleaning up polluted agricultural, military, and industrial sites. However, the intrinsic chemical and structural heterogeneity of natural samples poses a challenge for identifying individual metal species using bulk sensitive techniques, and recent advances in X-ray microprobe analytical techniques provide the spatial resolution that is needed to characterize these materials at the micron scale. In an effort toward this goal, we have examined how Zn and Ni are naturally sequestered in (Fe,Mn)-rich soil micronodules by the synergetic use of μ SXRF (Synchrotron-based X-Ray Fluorescence) and μ XRD (X-Ray Diffraction). X-ray microanalysis was used first to map the partitioning of these trace contaminants among coexisting mineral phases, then microdiffraction was applied to determine which mineral species the trace element is bound to.

EXPERIMENT

Several soil micronodules were prepared as 30 microns-thick thin sections adhered to a glass slide mount. Measurements were conducted on the 7.3.3 microdiffraction beamline in reflection geometry by inclining the sample to $6^\circ \theta$ [1]. At this angle, the lateral size of the illuminated area was 20×30 microns. Fluorescence maps were obtained by scanning the samples under a monochromatic beam ($E = 10$ keV) with a step size of $50 \mu\text{m}$ and a 5 sec per step integration time. μ XRD patterns were collected using a large area CCD camera and an exposure time of 10 to 20 min. The distance between the analyzed spot on the sample and CCD and the 2θ scale were precisely calibrated using the reflection peaks of quartz grains contained in the soil nodules.

RESULTS

Figures 1 and 2 show how laterally resolved μ SXRF and μ XRD data can be used to identify the partitioning of trace elements among coexisting mineral phases within their natural matrix. With μ SXRF the distribution of Fe, Mn, and Zn were determined, and it was found that Mn and Zn are closely associated in all examined nodules. Application of μ XRD within a number of Fe and Mn-rich regions showed that Fe is essentially speciated as goethite (αFeOOH) whereas two Mn species were positively identified, lithiophorite and birnessite. Lithiophorite and birnessite both have a layered structure, but a different chemical composition and stoichiometry of the Mn layer (Fig. 3). The lithiophorite structure consists of mixed MnO_2 and $\text{Al}(\text{OH})_3$ octahedral layers [2], whereas birnessite has a single MnO_2 layer structure in which Mn atoms are adsorbed in the interlayer space above and below vacant octahedral sites [3]. hkl reflections were successfully detected in the XRD patterns of minute birnessite grains, indicating the existence of coherently stacked MnO_2 layers, but generally only two-dimensional hk bands were detected, which is indicative of random stacking of Mn layers. XRD simulations are underway to determine the stacking mode, and therefore the interlayer structure, of the best crystallized grains. X-ray microanalyses of dozen of birnessite and lithiophorite grains showed that Ni was only associated with the latter mineral, whereas Zn was fractionated between the two Mn minerals. This observation suggests that Zn is bound to Mn layers,

since this structural unit is common to the two phyllosulfate species, and that Ni is bound to the Al layer of lithiophorite. This question, together with the uptake mechanism of Zn and Ni at the atomic-scale in these two phases, shall be addressed in forthcoming months by μ EXAFS. In summary, in recent years there has been a growing demand in μ SXRF and μ XAS (X-ray absorption spectroscopy) capabilities for studying trace contaminants in natural systems [4]. The results reported here provide a firm experimental demonstration of the great potential of completing these micro-analytical (μ SXRF) and micro-spectroscopic (μ XAS) analyses with application of a micro-structural tool (μ XRD) for advanced characterization of environmental systems.

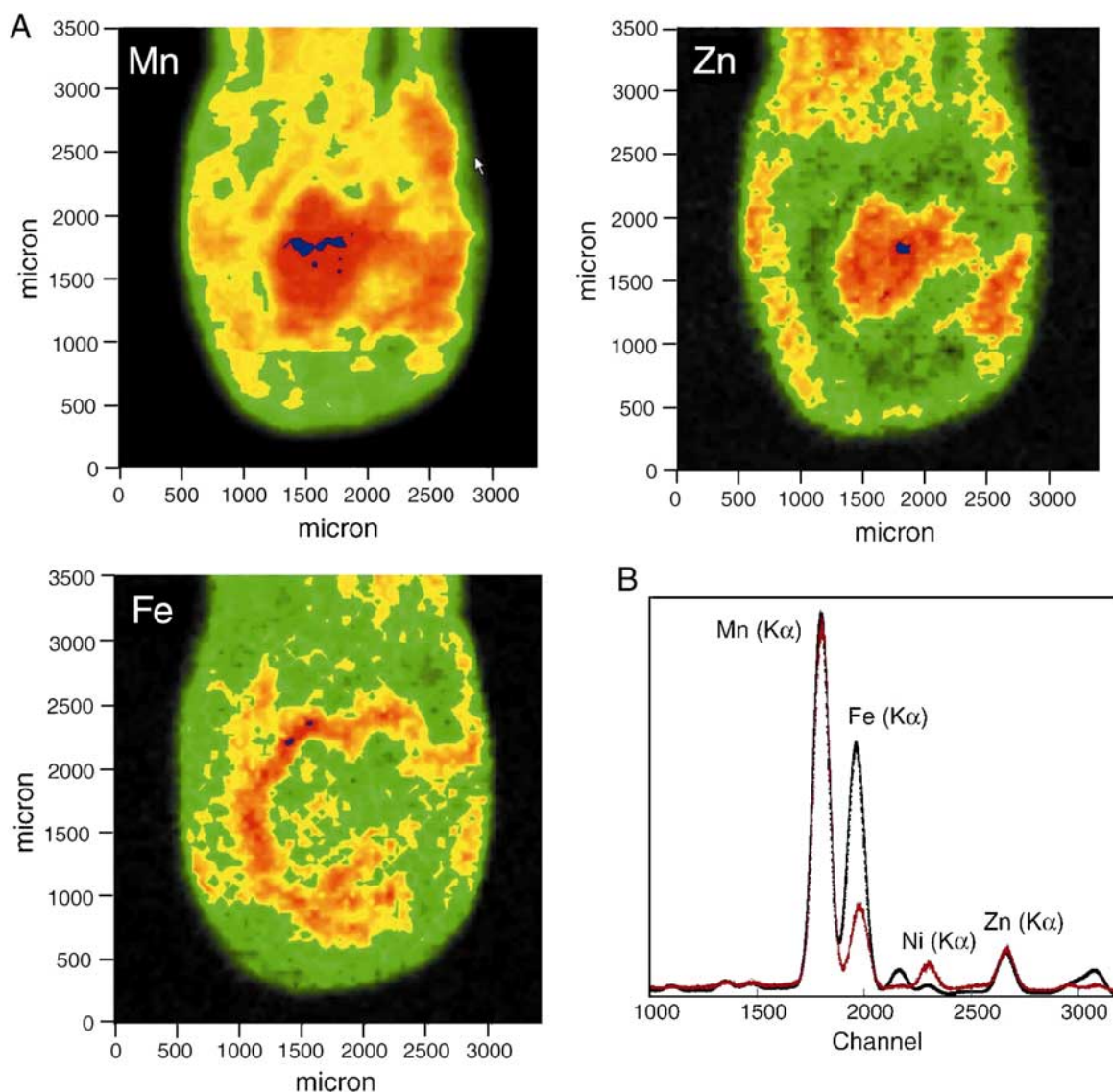


Figure 1. A) Distribution of Mn, Zn, and Fe in a soil micronodule. Zn is concentrated with Mn, essentially in the core region and to a lesser extent in the external part of the nodule. B) X-ray fluorescence spectra taken in the core region (red line) and in the external region (black line). Nickel is concentrated in the center of the nodule, whereas Zn follows the entire Mn contour map.

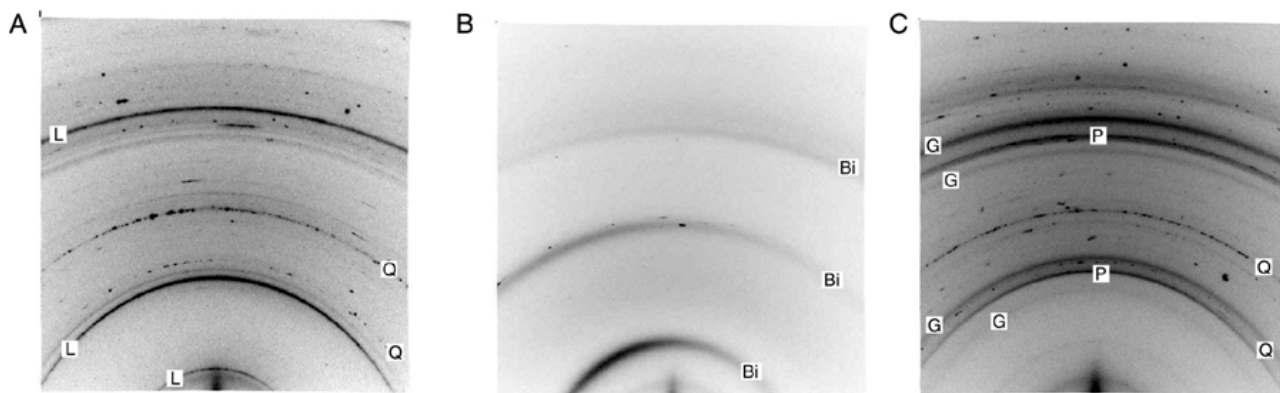


Figure 2. Three main types of microdiffractograms. A) Lithiophorite (L), predominantly present in the core region. B) Birnessite (Bi), predominantly present in Mn-containing area of the external region. C) Goethite (αFeOOH , G), detected in Fe-rich area, and phyllosilicates (P) forming a clayey matrix intimately mixed with iron oxides, but also with birnessite in most regions of the nodule. Q: quartz.

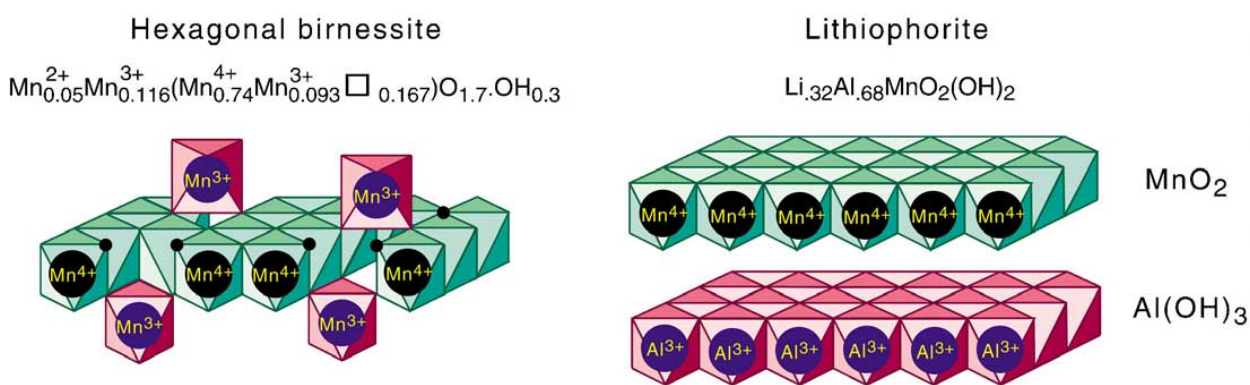


Figure 3. Structure of hexagonal birnessite and lithiophorite.

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